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STRUCTURE, ELECTROPHYSICAL, THERMAL AND MECHANICAL PROPERTIES OF POLYMER NANOCOMPOSITES BASED ON POLYVINYLIDENE FLUORIDE (PVDF) AND MULTI-WALLED CARBON NANOTUBES (MWCNT)

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Abstract. The polymer nanocomposites based on polyvinylidene fluoride (PVDF) and multi-walled carbon nanotubes (MWCNT) have been synthesized. The structure, electrophysical, thermal and mechanical properties of polymer nanocomposites were investigated. Have been established that at their lower content, carbon nanotubes play the role of structuring agent. As a result, the new polar groups and stable charge-trappings are created in the obtained nanocomposites, which in turn increases the value of dielectric permittivity of nanocomposites and enhances the polarizability of these materials. It was found that the incorporation of MWCNT nanoparticles into the polyvinylidene fluoride polymer matrix reduces the thermal resistance of nanocomposites. Have been determined that the introduction of multi-walled carbon nanotubes into the polymer caused a decrease in the elongation at break of nanocomposites to compare a pure PVDF matrix.

Keywords: *nanocomposite, polyvinilidenefluoride, polymer, nanoparticles, carbon nanotubes.*

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1. Introduction

Currently, one of the promising areas in polymer and materials science is the development and production of a new class of materials-polymer nanocomposites. The unique properties of these nanocomposites are not only due to the extremely small size of nanoparticles, but also due to the structural characteristics of the polymer matrix. The polymer matrix allows nanoparticles to be organized into supramolecular structures, which greatly enhances the inimitable properties of Nano sized particles. The polymer composite with filler in the form of nanoparticles dispersed in matrix are promising for use as new conductive, photosensitive, magnetic, catalytic, and other materials that combine the properties of both a polymer medium and filler. Such materials exhibit optical, catalytic, magnetic, and sensory properties that are unusual in comparison with bulk materials. The advantage of such means is that it is possible to obtain both systems with low concentrations of nanoparticles in a polymer matrix, and systems with high concentrations of interacting particles (Pomogilo *et al.*, 2000).

This paper is devoted to the experimental study of the structure, electrophysical, thermal and mechanical properties of nanocomposites based on the thermoplastic PVDF polymer and multi-walled carbon nanotubes (MWCNT), as well as to the identification of the relationship between changes in the properties and structure of these nanocomposites.

2. Experimental part

2.1. Materials and methods

Polyvinylidene 116luoride (PVDF) is a polar polymer that has a density of 1.78 g/cm^3 at 25ºC, melting point is at the T=177ºC, N,N-dimethylformamide (DMF) (99.8% chemically pure, Sigma-Aldrich). The MWCNT is product of the Sky-Spring nanomaterials (Lot 0554CA).

2.2. Preparation of PVDF/MWCNT nanocomposites

Polymer nanocomposites based on PVDF+MWCNT were obtained as follows: powders of polyvinylidene fluoride polymer are dissolved in an organic solvent of dimethylformamide (DMF). Then multi-walled carbon nanotubes were added to the dissolved polymer system and intensively mixed in a magnetic mixer at 40-50^{0}C for 4 hours. The resulting mixture is treated in a vacuum oven by complete evaporation of the solvent. Nanocomposite layers of different thicknesses were obtained using the hot pressing method under the pressure of 10 MPa at the melting temperature of PVDF.

2.3. Research methods

2.3.1. XRD analysis

To determine the crystalline structure of the PVDF and the nanocomposites, X-ray diffraction was used. The samples were evaluated in a diffractometer Rigaku Mini Flex 600 XRD, operated at a current intensity of 15 mA and a voltage of 30 kV to obtain the radiation corresponding to the Cu K-α at a longitude wave of 1.54056 Å. The scanning in the 2θ scale was from 10° to 100° with a sample velocity of 0.02°/s

2.3.2. Scanning electron microscopy (SEM)

The morphology of the polymer nanocomposites was determined by means of a scanning electron microscope model Jeol JSM-7600 F. Scanning was performed in secondary electron detecting (SEI) mode at an accelerating voltage of 15 kV and a working distance of 4.5 mm. Energy dispersive micro-X-ray analysis was performed using the device X-Max 50 (Oxford Instruments). In order to make their surface conductive, the samples were coated with the thin films of platinum using a sputtering technique.

2.3.3. Dielectric measurements

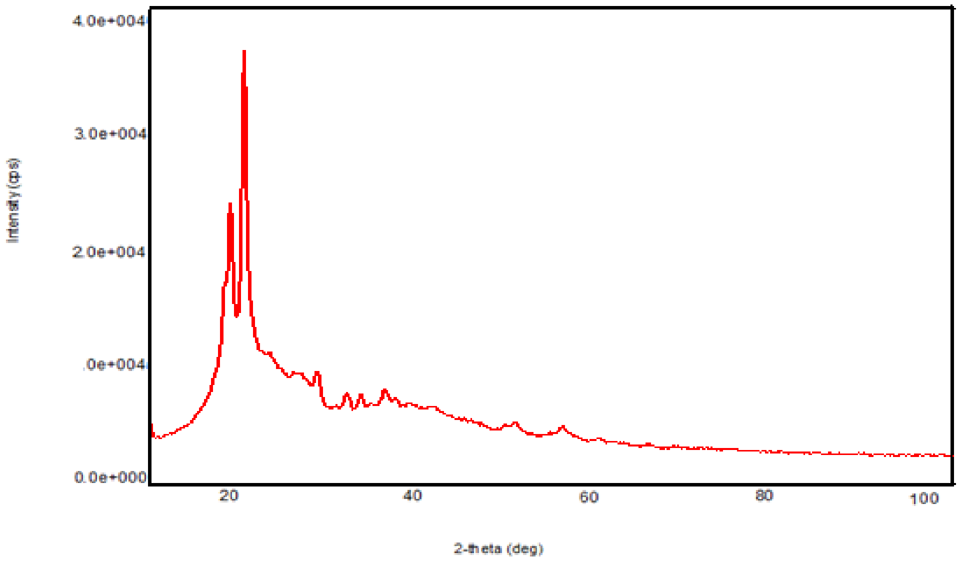
Measurement of the dielectric permittivity and dielectric loss tangent was conducted using immittance meter MNIPI E7-20 by applying a broadband meter E7-20 immittance. Were measured the frequency dependence of capacitance and dielectric loss at a temperature T=293 K in the frequency range f=25Hz-1MHz.

2.3.4. Thermogravimetric analysis (TGA)

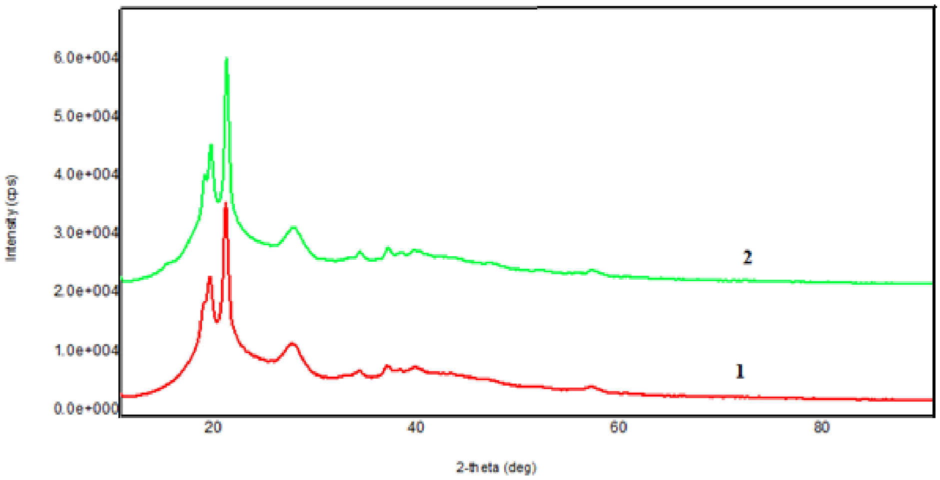
Thermogravimetric analysis of samples was performed using an SDT Q600 (TA Instruments) analyzer. Nanocomposites samples were heated from 30°C up to 650°C under a nitrogen flow rate of 100 mL/min and a heating rate of 10°C/min.

3. Results and discussions

Fig. 1 shows the diffractograms of polymer nanocomposites based on PVDF+MWCNT. In the diffraction pattern of PVDF, two intensive peaks are observed at 2θ =18.83° and 20.41°. These peaks are characteristic diffraction peaks of the α and β phases of PVDF, which correspond to 020 and 110 Muller indices, respectively, at the 2θ = 18.4^0 and 2θ = 20.80, known from the literature. It was established that the introduction of carbon nanotubes into the polymer matrix of PVDF leads to an increase in peak intensities at 2θ equals 18.71^0; 27.11^0 and 33.47^0, which correspond to the α crystalline phase of the PVDF polymer (Emplit *et al.*, 2017; Moniruzzaman & Winey, 2006; Ates *etal.*, 2017; Sahoo *et al.*, 2010; Kanoun *et al.*, 2021).



a)



b)

Fig.1. Diffraction patterns of PVDF *(a)* and polymer nanocomposites based on PVDF+MWCNT *(b)*: 1. PVDF+5%MWCNT; 2. PVDF+10%MWCNT

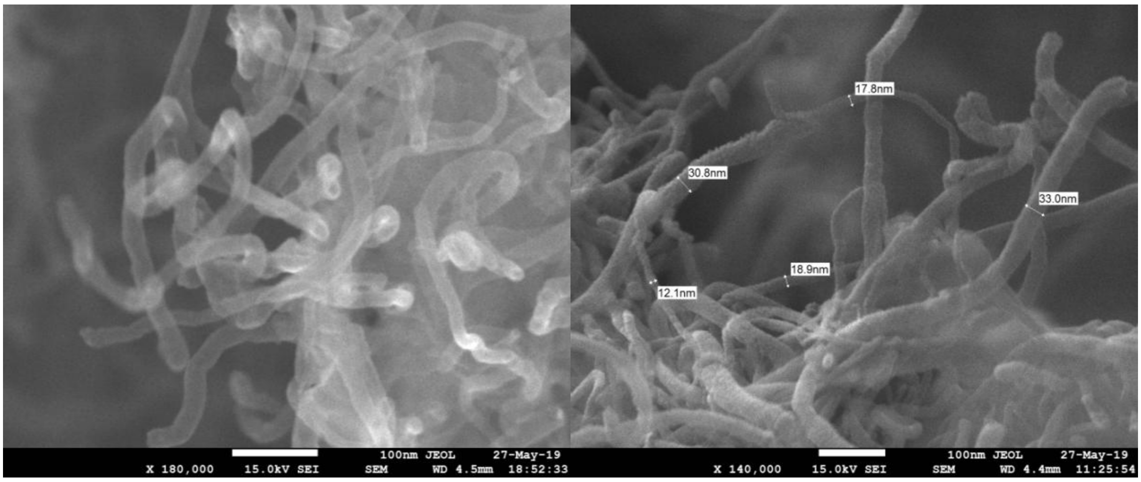


Fig.2. SEM images of PVDF/MWCNT based polymer nanocomposites

Fig.2 shows scanning electron microscopic (SEM) images of PVDF+MWCNT-based polymer nanocomposites. SEM images demonstrate that the diameter of carbon nanotubes in the polymer matrix is about 22-37 nm.

Fig.3 shows the energy-dispersive spectrum (EDS) of PVDF+MWCNT-based polymer nanocomposites. As can be seen from the EDS spectrum, the polymer nanocomposite contains only carbon nanotubes and polymer. Signal of any additional impurities is not detected. The Ni element comes from the sample substrate.

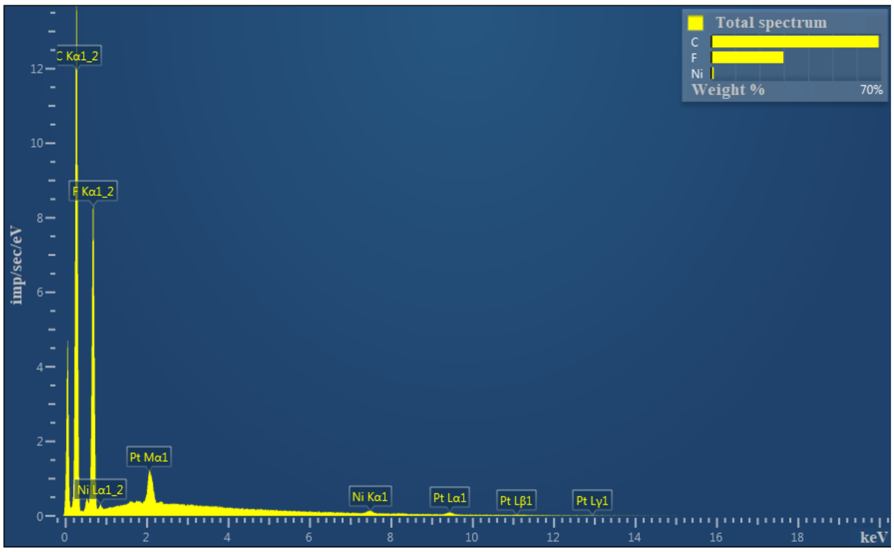


Fig. 3. Energy-dispersive spectrum of PVDF+MWCNT based nanocomposites

Fig.4 shows the frequency dependence of the dielectric constant (ε) of PVDF+MWCNT based nanocomposites. As can be seen from Fig. 4, the dielectric constant begins to decrease with increasing frequency. The value of the dielectric constant of nanocomposites based on PVDF+MWCNT increases up to 10% content of carbon nanotubes compared to pure PVDF (for PVDF ε = 9-11). The increase in carbon nanotubes by up to 10% is explained by the fact that this amount of carbon nanotubes plays the role of a structuring agent in the polymeric matrix. The increase in the value of the dielectric constant of polymer nanocomposites by up to 10% of carbon nanotubes is explained by the increase in the polarization capacity of nanocomposite materials up to this content.

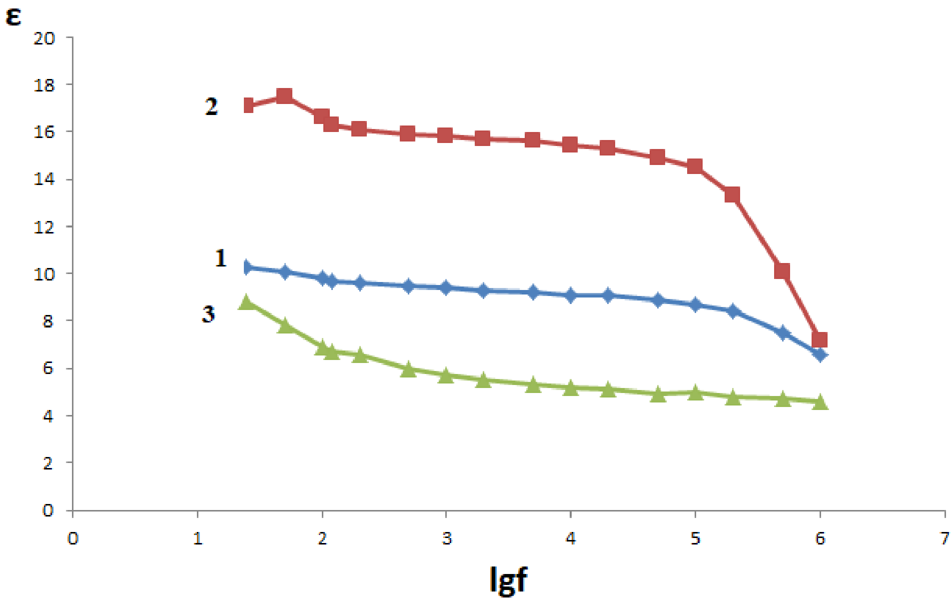


Fig. 4. Frequency dependence of dielectric constant of PVDF+MWCNT-based polymer nanocomposites: 1. PVDF+5%MWCNT; 2. PVDF+10%MWCNT; 3. PVDF+20%MWCNT

Fig.5 shows the frequency dependence of the dielectric loss angle tangent (tgδ) of PVDF+MWCNT based polymer nanocomposites. As can be seen from Fig.5, tgδ begins to decrease with increasing of the frequency and then increases at higher frequencies. An increase the tgδ values at high frequencies is explained by an increase in relaxation processes and energy dissipation in these systems. At high frequencies, the value of molecular vibrations coincides with the frequency of the measuring system. This fact leads to a sharp increase in energy dissipation. As a result, the raise of the tgδ value and electrical conductivity in an alternating field is observed (Liu *et al.*, 2018; Gojny *et al.*, 2006; Mohiuddin & Hoa, 2013; Maiti *et al.*,2013; Zare & Rhee, 2017; Ramazanov *et al.*, 2018).

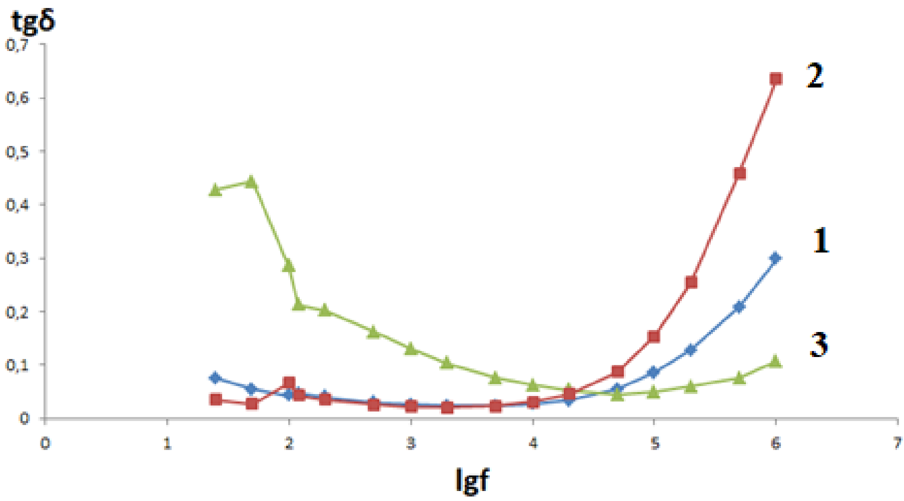


Fig. 5. Frequency dependence of dielectric loss of PVDF+MWCNT based polymer nanocomposites: 1. PVDF+5%MWCNT; 2. PVDF+10%MWCNT; 3. PVDF+20% MWCNT

The thermal properties of PVDF+MWCNT-based polymer nanocomposites have been studied. Fig.6 shows the thermogravimetric analysis (TGA) curves of PVDF+MWCNT-based polymer nanocomposites. As can be seen from the TGA curves, the initial temperature for thermal- oxidative destruction for PVDF is 429^0C. When MWCNT are introduced into the PVDF matrix, the initial thermal-oxidative destruction temperature of nanocomposites shifts to lower temperatures. The initial temperature of thermal-oxidative destruction for PVDF+5% MWCNT and PVDF+10%MWCNT nanocomposite is 406.53^0C and 400^0C, respectively. Thus, it was found that the incorporation of MWCNT nanoparticles the polyvinylidene fluoride polymer matrix reduces the thermal resistance of PVDF+MWCNT nanocomposites (Maharramov *et al.*, 2017; Ramazanov *et al.*, 2018; Ramazanov *et al.*, 2016).

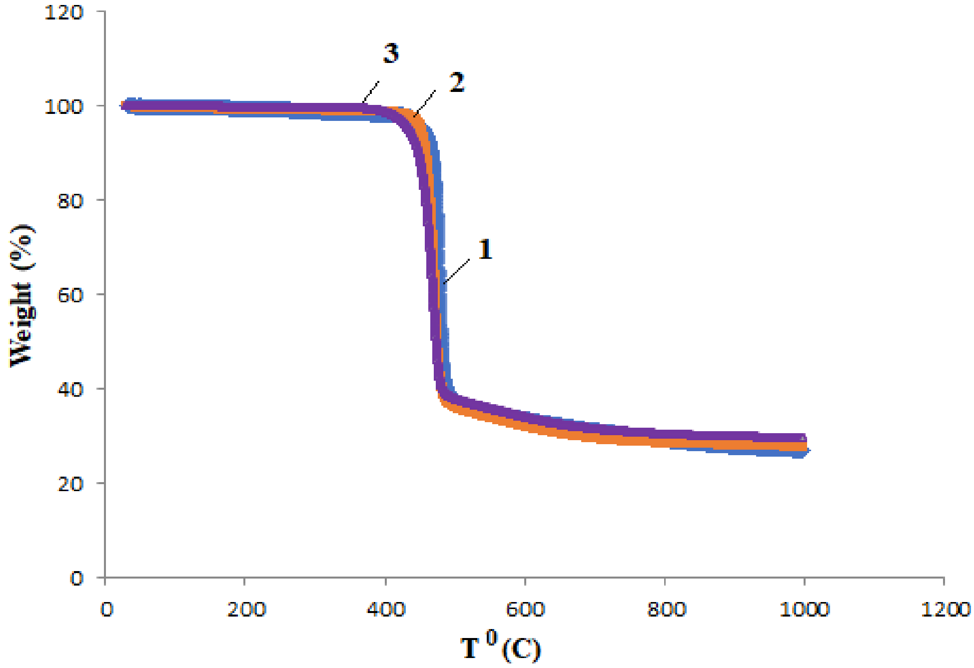


Fig. 6. TGA curves of PVDF+MWCNT-based polymer nanocomposites: 1. PVDF; 2. PVDF+5% MWCNT, PVDF+10% MWCNT

All results of thermogravimetric analysis of polymer nanocomposites are shown in Table 1.

Table 1. Influence of MWCNT on thermos-stability of PVDF-based nanocomposites.

Composition of nanocomposites	Initial thermo-oxidative destruction temperature (°C)	Integral temperature (°C)	Final thermo destruction temperature (°C)
PVDF	429	482,68	940,99
PVDF+5%MWCNT	406,53	474,38	996,89
PVDF+10% MWCNT	400	473,18	996,87

Table 1 shows the initial temperature, integral temperature (the temperature at which sample's destruction rich almost to 50% and the final temperature of thermal-oxidative destruction of PVDF and PVDF+MWCNT based nanocomposites.

The mechanical properties of polymer nanocomposites based on PVDF+MWCNT were also studied. Fig.7 shows the stress-strain curves of nanocomposites based on PVDF+MWCNT. Stress-strain curves of nanocomposites were obtained by using Zwick/Roell Z010 equipment (Zwick/Roell GmbH, Germany). To carry out the measurement, specimens cut in a certain shape were subjected to tension under the action of a force equal to 1 kN at a speed of 10 mm/min.

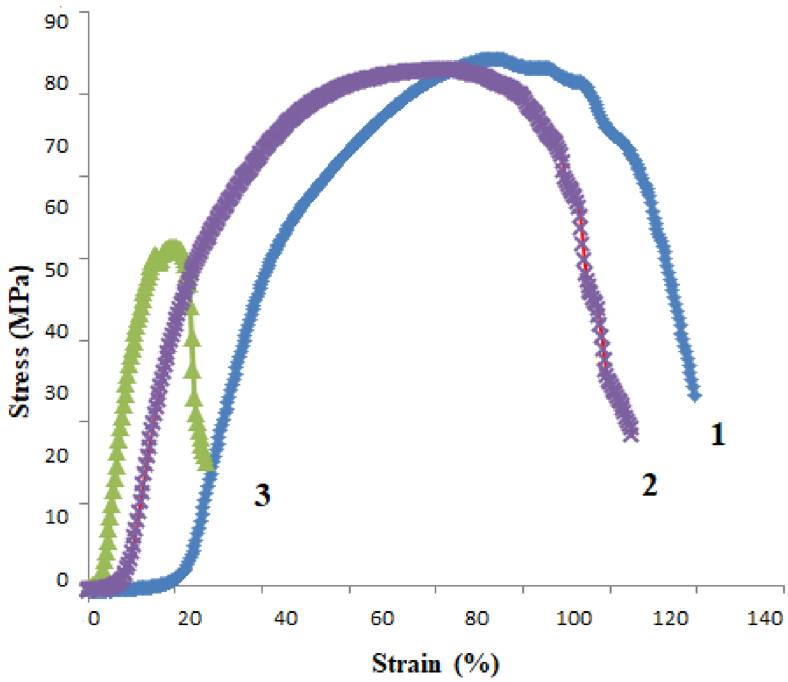


Fig. 7. Stress-strain curves of nanocomposites of PVDF+MWCNT-based polymer nanocomposites: 1. PVDF; 2. PVDF+5% MWCNT, PVDF+10% MWCNT

It was found that the introduction of multi-walled carbon nanotubes into the matrix caused a decrease in the nanocomposites'elongation at the break in comparison with a pure PVDF. However, at a low 5% content of carbon nanotubes in the polymer, nanocomposites still exhibit high plastic deformation (Maharramov *et al*., 2017).

4. Conclusion

Have been synthesized of polymer nanocomposites based on polyvinilidenefluoride (PVDF) and multi-walled carbon nanotubes (MWCNT). The structure, electrophysical, thermal and mechanical properties of polymer nanocomposites were investigated. Have been established that at lower content, carbon nanotubes play the role of structuring agent. As a result, the new polar groups and stable charge-trappings are created in the obtained nanocomposites, which in turn increases the value of dielectric permittivity of nanocomposites and enhances the polarizability of these materials. It was found that the incorporation of MWCNT nanoparticles into the polyvinylidene fluoride polymer matrix reduces the thermal resistance of polyvinylidene fluoride-based nanocomposites. Have been determined that the introduction of multi-walled carbon nanotubes into the polymer caused a decrease in the elongation at break of nanocomposites in comparison with a pure PVDF matrix.

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